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In-situ characterization of Ga_2O passivation of $In_{0.53}Ga_{0.47}As$ prior to high-k dielectric atomic layer deposition

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Ga_2O interfacial passivation layers (IPLs) on $In_{0.53}Ga_{0.47}As$ are investigated using *in-situ* monochromatic x-ray photoelectron spectroscopy. The oxide is entirely composed of Ga_2O when deposited with an effusion cell temperature of 1500 °C and substrate temperature of 425 °C. The growth on $In_{0.53}Ga_{0.47}As$ reveals slight chemical modification of the surface. The Ga_2O behavior and ability to protect the III-V surface are observed following Al_2O_3 deposition by atomic layer deposition following each precursor pulse. Al_2O_3 growth by trimethyl-Al (TMA) and water reveals that the IPL undergoes the "clean-up" effect following TMA exposures causing As-As bonding formation resulting in a high interface state density. © *2011 American Institute of Physics*. [doi:10.1063/1.3615666]

Research on III-V substrates for metal oxide semiconductor field effect transistor (MOSFET) applications has focused on improving the quality of the insulator/substrate interface since it represents a major obstacle for widespread adaptation of this material system in future technology nodes. The defect (trap) density (D_{it}) of this interface can be quite high, pinning the Fermi level and resulting in significantly degraded transport properties.[1] Recent theoretical studies[2,3] and previous experimental work[4] indicate that the suppression of particular interfacial oxidation states can reduce this D_{it} and improve the performance of III-V based materials. Strategies such as Si (Refs. 5 and 6) and Ge (Ref. 7) interfacial passivation layers (IPLs) and Gd containing gadolinium gallium oxide (GGO) interfacial oxides[8–10] have been employed in an attempt to control the chemical species present at the interface. Previous work has indicated the presence of Ga_2O at the interface of devices showing improved capacitance-voltage (CV) and drain current-gate voltage (I_d-V_g) characteristics on GaAs(100).[4] Additionally, first principles calculations[2,11] as well as scanning tunneling microscopy results[16] indicate that Ga_2O-like interfacial bonding on GaAs(100) does not result in gap states. Previous reports of molecular beam epitaxy (MBE) grown GGO on InGaAs have reported the inclusion of a Ga_2O "template layer"[12] that deposits initially on the InGaAs surface before the full stoichiometric GGO is formed. D_{it} extraction from CV and conductance data indicate an improved interface, at least in terms of midgap D_{it} levels.[12–14] However, in each of those studies, the MBE deposited dielectric thickness is on the order of 6 to 10 nm or more, precluding their use in scaled devices. In this work, thin (~0.3 nm) MBE deposited Ga_2O is investigated as a passivation layer prior to high-k atomic layer deposition (ALD) in an attempt to protect the bulk InGaAs from further oxidation and the formation of deleterious Ga dangling bonds and As-As bonds. The ALD conditions included trimethyl-Al (TMA) and H_2O pulse times of 0.1 s, N_2 purge times of 4 s, and gas flow rates of 200 sccm each. The substrate temperature was maintained at 300 °C throughout the ALD process.

Ga_2O was grown from a high temperature effusion source from polycrystalline Ga_2O_3 contained in a custom iridium crucible. The evaporation of polycrystalline Ga_2O_3 at high temperatures is expected to result in Ga_2O deposition[15,16] since bulk Ga_2O_3 decomposes to form Ga_2O and O_2. Fortuitously, the sticking coefficient of Ga_2O on GaAs is six orders of magnitude larger than that of O_2 which should result in pure Ga_2O growth.[17]

The Ga_2O is grown on 300 nm thick $1 \times 10^{17}/cm^3$ p-type doped $In_{0.53}Ga_{0.47}As$ (100) on a $1 \times 10^{18}/cm^3$ p-type doped InP substrate following the *in-situ* thermal desorption of a protective 50 nm thick As-capping layer. Due to the ~450 °C decapping temperature, electron diffraction (not shown) indicates a mixed $(2 \times 4)/(4 \times 2)$ surface reconstruction as noted previously by Shen *et al.*[18] and serves as a control sample to establish the monochromatic x-ray photoelectron (XPS) spectra shape on the atomically clean surface that may be utilized for the careful spectral deconvolution performed here.[4,19] The Ga_2O films were deposited at 1350 °C–1700 °C effusion cell temperatures (T_{source}), while the substrate temperature was either room temperature or 425 °C. The effect of effusion cell and substrate temperature on the chemical composition of the Ga_2O IPL is shown in Fig. 1 through the surface sensitive[20] Ga $2p_{3/2}$ spectra. Following a 2 min deposition at $T_{source} = 1350$ °C onto a room temperature substrate, a convoluted spectrum (Fig. 1(a)) with the expected bulk substrate bonding, the Ga_2O (Ga^{1+}) bonding,[4] metallic gallium (Ga^o, e.g., Ga-Ga bonding) and Ga_2O_3 (Ga^{3+}) bonding is detected. This indicates that at lower T_{source}, the molecular beam chemistry is not simply Ga_2O and O_2 but possibly contains metallic Ga which then reacts with the O_2 also liberated by the source to form the additional states. If the deposition is performed with the same $T_{source} = 1350$ °C and the elevated substrate temperature $T_{sub} = 425$ °C, only the bulk Ga-As state remains.

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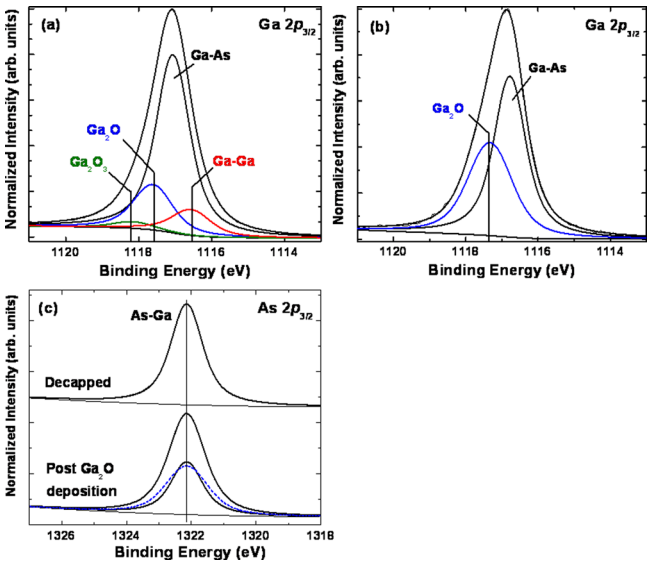

FIG. 1. (Color online) (a) Ga $2p_{3/2}$ core-level XPS spectrum for deposition ($T_{source} = 1350\,°C$) on a substrate maintained at room temperature. The molecular beam chemistry at this T_{source} results in the detection of metallic Ga and the Ga^{1+} and Ga^{3+} oxidation states. (b) Ga $2p_{3/2}$ XPS spectrum of an optimized Ga_2O deposition ($T_{source} = 1500\,°C$) with a substrate temperature of 425 °C. Only Ga_2O is deposited. (c) As $2p_{3/2}$ spectrum showing the bulk As-Ga peak following As decapping and also a slightly broadened peak indicating increased disorder due to Ga_2O disruption of the As terminated surface.

However, if the effusion cell temperature is raised to $T_{source} = 1500\,°C$ (deposition rate ~0.1 nm/min), only Ga^{1+} bonding is detected in addition to the bulk Ga-As (Fig. 1(b)) indicating that Ga_2O is the deposited species coming from the molecular beam. It should be noted that depositions were also performed at $T_{source} < 1300\,°C$ and as high as 1700 °C (not shown). The low temperature ranges resulted in no detectable depositions while the higher temperatures resulted in overly rapid deposition rates. Hence, the optimal deposition conditions for thin IPLs were chosen ($T_{source} = 1500\,°C$, $T_{sub} = 425\,°C$). For the half-cycle studies and the correlated device fabrication, a ~0.3 nm Ga_2O interface passivation layer was deposited.

As suggested previously,[21] the deposition of Ga_2O on InGaAs and GaAs would ideally result in Ga_2O units bonding to the As at the surface or on row edges.[19] This surface reaction should be difficult to detect using XPS with the As spectrum as this would manifest as As-Ga bonding at a nearly identical binding energy as that of the bulk As-Ga from the substrate. The As $2p_{3/2}$ spectra in Fig. 1(c), however, displays a broadening of the peak as compared to the spectrum of a decapped pristine bulk substrate and is attributed to the slight disruption of the surface As following Ga_2O deposition creating an increased level of As-Ga bond disorder. This can be thought of as two convoluted As-Ga signals, one arising from the bulk pristine crystal surface and the other from the Ga_2O attachment to the surface As. The spectrum is therefore shown with two peaks having similar binding energies but different Gaussian widths. It is noted that there is no As-O detected following these depositions or the subsequent ALD Al_2O_3 described later. Additionally, the In $3d_{5/2}$ spectrum displays a change in the peak profile following Ga_2O deposition (not shown). This change occurs on the high binding energy side of the bulk peak and may include the oxidation of In. However, due to the difficulty in deconvoluting the In spectrum due to inherent asymmetries,[22] the root cause of this surface alteration requires further study.

In order to evaluate the stability of the Ga_2O IPL during ALD depositions, the As $2p_{3/2}$ and Ga $2p_{3/2}$ spectra for an $In_{0.53}Ga_{0.47}As$ sample are shown in Fig. 2(a) following each individual TMA and H_2O precursor pulses as well as following the deposition of a 1 nm Al_2O_3 film using methods described previously.[22–24] Prior to the first TMA exposure, the sample is inserted into the ALD reactor for 30 min in order to determine the effect of temperature and any residual species (base pressure $\sim 10^{-3}$ mbar). These spectra are identical to the spectra before the ALD exposure indicating that the Ga_2O layer is stable in the ALD reactor environment prior to precursor exposure.

Exposure to TMA results in a slight reduction of the Ga_2O intensity as has been shown previously with (non-MBE) native Ga-oxides via the cleanup effect.[22–24] In addition, there is the emergence of As-As (As^o) bonding as well which may be responsible for mid-gap D_{it}.[2,3] Exposure to the first water pulse does not change the chemical configuration as both the As and Ga regions are identical to the previous spectra. Unlike similar experiments on III-V oxides that show completed reactions following the first TMA pulse,[23,24] this Ga_2O IPL undergoes a second reduction following further TMA exposures and even some Ga_2O regrowth following water pulses up to the final 1 nm Al_2O_3 ALD film. There is no interfacial Ga_2O_3 detected in these experiments which is one of the requirements to reduce interfacial traps.[4] However, with each cycle,

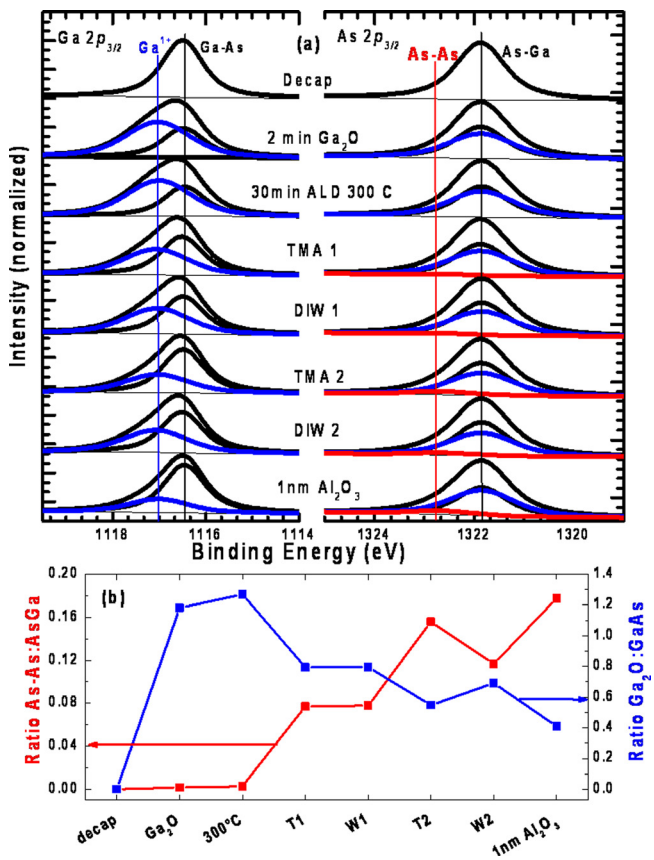

FIG. 2. (Color online) (a) XPS spectra showing the progression of interfacial species following ALD deposition on the Ga_2O passivation layer. (b) Ratios indicating that Ga_2O gets reduced and As-As bonding concentration gradually increases with each TMA pulse.

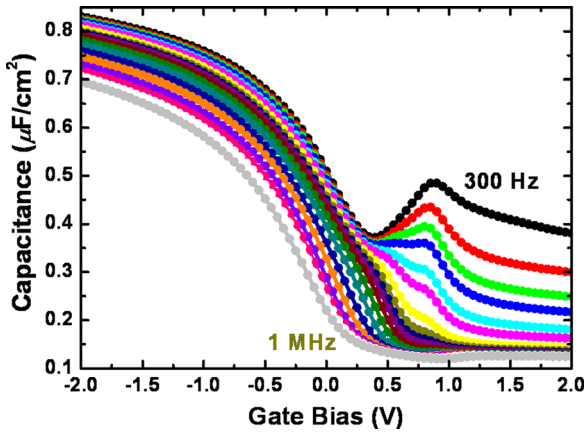

FIG. 3. (Color online) Multi-frequency (300 Hz to 1 MHz) C-V characteristics of p-$In_{0.53}Ga_{0.47}As/Ga_2O/Al_2O_3$/Ni-Au gate stack. The capacitor area was $\sim 3.5 \times 10^{-8}$ m^2. The frequency dispersion is indicative of high D_{it} most likely arising from the formation of As-As bonding during ALD growth.

the As-As bond concentration continues to increase (Fig. 2(b)) indicating that the Ga_2O IPL is ineffective at preventing the gradual formation of this chemical state during ALD growth. It is noted, however, that the initial formation of such bonding is near the detection limit, in contrast to prior studies without such MBE Ga_2O interfacial layers present where chemical preparations were employed.[23,24]

To investigate the electrical characteristics of these interfaces, MOS capacitors were fabricated on identical $In_{0.53}Ga_{0.47}As$ substrates. The capacitor dielectric stack consisted of the Ga_2O IPL followed by 8 nm of Al_2O_3 with a gate metal of Ni/Au. As can be seen in the C-V characteristics (Fig. 3), there is a significant amount of frequency dispersion over the entire bias range examined, indicative of high D_{it} and Fermi level pinning. If we assume that the As-antisite density[25,26] is below the limit of detection in the near surface region sampled by XPS, we speculate that this D_{it} is related to the As-As dimer bonding that arises during exposure to the ALD deposition and may prevent Ga_2O from being an effective passivation layer for such III-V channel materials under these conditions.

The results demonstrate that growth of pure Ga_2O layers from polycrystalline Ga_2O_3 occurs at a T_{source} of 1500 °C and a T_{sub} of 425 °C. The grown IPL is stable under standard ALD reactor conditions and hence possibly appropriate for subsequent *ex-situ* fabrication as well. However, this Ga_2O IPL is not impervious to modifications by TMA and water exposure during the high-*k* atomic layer deposition. Under these conditions, the IPL gets significantly reduced and results in the formation of interfacial As-As bonding, high D_{it}, and poor C-V characteristics.

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